EFFECTS OF CARBON DIOXIDE GAS ON FLAMMABILITY LIMITS OF LPG

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ABSTRACT

Liquefied petroleum gas or LPG has well acknowledged as an attractive source of fuel in these centuries as it has provided us evidence to be the most effective and environmental friendly among all other fuel existed. However, like the other fuel, LPG also has its own benefits and drawbacks at when it is inadequately treated can be destructive to us. After knowing the characteristics of LPG and recognizing suitable ways of reducing risks in storage, handling and transportation of it, an appropriately planned experiment has been carried out. Specifically, this study is conducted to study the effect of carbon dioxide (CO_2) to the Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) of LPG. LFL and UFL create a range at which explosion may occur to any flammable substance. By adding diluents (in this case is CO_2) to the LPG-air mixture, the range was predicted to be narrowed down because the role of diluents to the mixture is to reduce the concentration of oxygen (O_2) existed in the mixture to a level where explosion can be stopped. The most proper equipment to be used in order to achieve the objective of the study is the 20-L-Explosion Vessel. Only by using this high-tech equipment- the experiments, which involving explosion, can be safely performed. In the experiment, different volume percentage of CO_2 was added in the pre-mixed LPG - air mixture. Three sets of experiments were done in order to compare the effect of CO_2 addition in the pre-mixed LPG - air mixture towards its flammability limit respectively. Fortunately, the results were moderately following the theories where the range of flammability limit of LPG - air mixture was fruitfully reduced from 4.2 % vol. To 3 % vol. of LPG.

ABSTRAK

Gas petroleum cecair atau LPG telah diperakui sebagai sumber bahan api yang menarik dalam abad ini kerana ia telah membuktikan keberkesanannya selain lebih mesra alam melampaui semua bahan api lain. Walau bagaimanapun, seperti bahan api lain, LPG juga mempunyai kebaikan dan keburukan di mana ia mampu merosakkan dan membahayakan kita jika tidak digunakan dengan baik. Setelah mengetahui ciri-ciri LPG dan mengenalpasti cara yang sesuai untuk mengurangkan risiko dalam penyimpanan, pengendalian dan pengangkutannya, eksperimen yang bersesuaian telah dijalankan. Secara khususnya, kajian ini dijalankan untuk mengkaji kesan karbon dioksida (CO_2) terhadap Had Kemudahbakaran Bawah (LFL) dan Had Kemudahbakaran Atas (UFL) LPG. LFL dan UFL mewujudkan julat di mana letupan boleh berlaku kepada apa-apa bahan yang mudah terbakar. Dengan menambah perencat (dalam kes ini adalah CO_2) ke dalam campuran LPG dan udara, julat ini diramalkan akan menjadi semakin mengecil kerana peranan perencat ialah untuk mengurangkan kepekatan oksigen (O_2) yang wujud di dalam campuran hingga ke tahap di mana letupan boleh dihentikan. Peralatan yang sesuai digunakan untuk mencapai objektif kajian ini ialah ‘20-L-Explosion Vessel’. Hanya dengan menggunakan peralatan berteknologi tinggi ini,, eksperimen yang melibatkan letupan, boleh dilaksanakan dengan selamat. Dalam eksperimen ini, peratusan isipadu CO_2 yang ditambah ke dalam pra-campuran LPG dan udara telah ditetapkan. Tiga set eksperimen telah dilakukan untuk membandingkan kesan tambahan CO_2 dalam pra-campuran LPG dan udara yang mampu membawanya ke arah had kemudahbakaran masing-masing. Keputusan daripada eksperimen yang telah dijalankan adalah sederhana mengikut teori-teori mengenai had kemudahbakaran campuran LPG dan udara di mana had kemudahbakarannya dapat dikurangkan dari 4 % isipadu kepada 3 % isipadu LPG.

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LIST OF ABBREVIATIONS

Ar	-	Argon
CH_4	-	Methane
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
LEL	-	Lower Explosive Limit
LFL	-	Lower Flammability Limit
LPG	-	Liquefied Peroleum Gas
MS	-	Malaysia Standard
Ne	-	Neon
NO_x	-	Nitrogen Oxide
N_2	-	Nitrogen
O_2	-	Oxygen
P_{ex}	-	Explosion Overpressure
P_m	-	Corrected Explosion Overpressure
P_{max}	-	Pressures Generated by The Closed Gas
t_d	-	Time-Delay Of the Outlet Valve
t_v	-	Ignition Delay Time
UEL	-	Upper Explosive Limit
UFL	-	Upper Flammability Limit
Xe	-	Xenon

LIST OF SYMBOLS

^{o}C	-	Degree celcius
barg	-	Bar gauge
kL	-	Kilo litre
kg	-	Kilo gram
kPa	-	Kilo pascal
L	-	Litre
ppm	-	Part per million
Re	-	Reynold's number

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

When mentioning about Liquefied Petroleum Gas (LPG), one must have imagined the usage of this fuel as a power source to everyday transportations such as cars, motorcycles and buses. Less realized by public, LPG has also been used primarily in empowering industrial sectors. For instance, in Ceramic and Glass Industry, LPG has been a far better-quality and extra clean fuel in eliminating obstacles during the melting process. Glass melting in this industry is a huge operation and involves numerous chemical reactions which occur during the process where LPG is the best choice of fuel because it enhances the product quality thereby reducing technical problems related to the manufacturing activity. Additionally, LPG is also the most idyllic fuel for production of food by Agriculture and Animal Husbandry. Drying of crops and other farm products require a clean and sulphur free fuel for drying activity to avoid any transfer of bad taste or smell to the dried crops. LPG in the farming industry can be used for examples in cereal drying, flame cultivation, soil conditioning and livestock farming ("LPG Application: Farming Industry",n.d).

Above all the spectacular uses of LPG, it is actually quite a risky fuel to deal with. Accidents involving LPG is sometimes unpredictable. LPG in cylinder vessel may leak as a gas or a liquid. If the liquid leaks it will rapidly evaporate and form a rather large cloud of gas which will drop to the ground, as it is heavier than air. LPG vapors can run for long distances along the ground and can assemble in drains or basements. When the gas meets a source of ignition it can burn or worse, explode. As liquid LPG is a fast evaporates substance, it can cause cold burns to the skin and it can act as an asphyxiant at high concentrations (Health and Safety Authority, 2011).

Realizing on how LPG can bring many unforeseen hazards to human, some initiatives should be taken to help reducing the risk of handling, processing and storing of it. One of the methods that is quite reliable and attract the engineers' interests to study further on is the addition of inert gas in the LPG itself. This process is usually addressed as inerting. It is done basically to protect a storage system (usually tanks and cylinder vessels) from exploding by keeping the oxygen content low. Conceptually, inerting will result in an increment in the Lower Flammability Limit (LFL) and decrease in the Upper Flammability Limit (UFL) which in other words, reduce the range of flammability of a flammable gas ("Standard for Inert Gas Systems", 1984).

Nitrogen (N_2) and carbon dioxide (CO_2) are examples of inert gases typically used for this purpose. As for this study, CO_2 has been chosen. According to Li *et al.* (2010), the usage of CO_2 gas as diluents in any flammable gas was proved to be working out. It is believed that CO_2 gas may decrease the explosion area of a flammable gas after it is added into the mixture of that gas with air.

1.2 PROBLEM STATEMENT

In 28 September 2011, there was an explosion and fire involving LPG happened in one of the premier shopping malls in Subang Jaya. The incident was traced by the accidental escape of the LPG from one of the food retail outlets on the lower ground floor early in the morning at about 3.45 am on that very day. Flash fire was noticed during the explosion and it was reported that there were two persons who were on the ground floor had been thrown off and landed on their backs some distance away. It was also reported that another two security guards who were at the control room at the level P1 car park were slightly injured by fallen debris (Department of Occupational Safety and Health, 2011).

The incident described is one of many other incidents happened involving LPG that leaved hideous impacts including deaths and injuries. Just like any other flammable gases, LPG explosions occur within the flammability limits of its substance. Diluents such as CO_2 and N_2 can help reducing the risks of an explosion of flammable substances by manipulating their flammability limits. This is why the flammability characteristics of LPG are very important when it comes to deal with storage, handling and transportation of this gas.

Thus, many studies and experiments have been performed in order to study and understand this special characteristic of LPG and how exploiting the usage of diluents may regulate its flammability limits. This continuing effort is very important to enhance safety.

1.3 OBJECTIVE OF STUDY

a) To study the effect of CO_2 as a diluents to the LFL and UFL of LPG.

1.4 SCOPE OF STUDY

This study has been conducted based on three main variables:

a) Manipulated Variables:-
Manipulated variables are the variables that have to be adjusted to obtain the desired results. In this research, the variable that has been manipulated was the percentage of CO_2 in the LPG-air mixture used. This percentage was based on volume of CO_2 over summation of CO_2 and LPG volume. This percentage must not exceed 15 % to avoid overloading of diluents and errors in results obtained.

b) Constant Variables:-

Constant variables are the parameters of the research. These variables must be fixed to avoid disturbances or errors during the experiment. The significant variables that have been decided to be the constant variables are the operating temperature and pressure. The temperature was constantly at 20 ^{o}C while pressure was maintained at 1 bar absolute.

c) Controlled Variables:-

Superior attention must be given to the controlled variables as they are the fundamentals for an experiment. They lead the experiment and showed how the manipulated variables should be varied in order to get desired results. In this case, the controlled variables were the UFL and LFL of LPG.

1.5 RATIONALE AND SIGNIFICANCE OF STUDY

As diluents, CO_2 may help to reduce the concentration of oxygen (O_2) in a fuel-air mixture. Theoretically, when the concentration of O_2 is reduced, the possibilities of explosion to occur are reducing too. In other words, the lower the O_2 concentration in fuel-air mixture, the fewer potential it has to be exploded. Besides that, exclusion of O_2 from spaces in storage tanks and vessels can also protect against the risks of unwanted chemical reactions with the stored liquid and corrosion of the storage container (BP Group Engineering Standards Forum, 1992).

Explosion, similar to combustion, may only be sustained if the heat released due to combustion is greater than that absorbed by the surroundings. It needs O_2, ignition source and flammable gas as the essential elements for the process. Exclusion of O_2 from spaces in storage tanks and vessels protects against the risks of fire and explosion, unwanted chemical reactions with the stored liquid, and corrosion of the storage container (Kasmani, 2011).

Therefore, the significance of this study was to reduce one of these elements (in this case O_2) by finding the most suitable amount of CO_2 to be added in the LPG-air mixture with the intention of changing its LFL and UFL to a safer level where possibilities of explosion to take place was minimum.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Storage, handling and transporting of Liquefied Petroleum Gas (LPG) can be very fussy because there are quite a number of procedures to be followed. No matter where are these process take place, there are always a guide or a standard to be referred based on certain situations. But, above all this, proper procedures for the handling, storage and transportation process is very important to keep away from unwanted disaster such as explosion (BP Group Engineering Standards Forum, 1992).

LPG, as well known by us, is usually stored and transported in cylinder vessels to meet up with just about the entire of its end consumers. The pressure inside each vessel is the vapor pressure for propane and butane mix at surrounding temperature. By using Figure 2.1, the vapor pressure of LPG can be estimated at surroundings' temperature range of -40 ^{o}C to 60 ^{o}C. However, this figure is only valid for small scale LPG cylinder which usually used by domestic consumers.

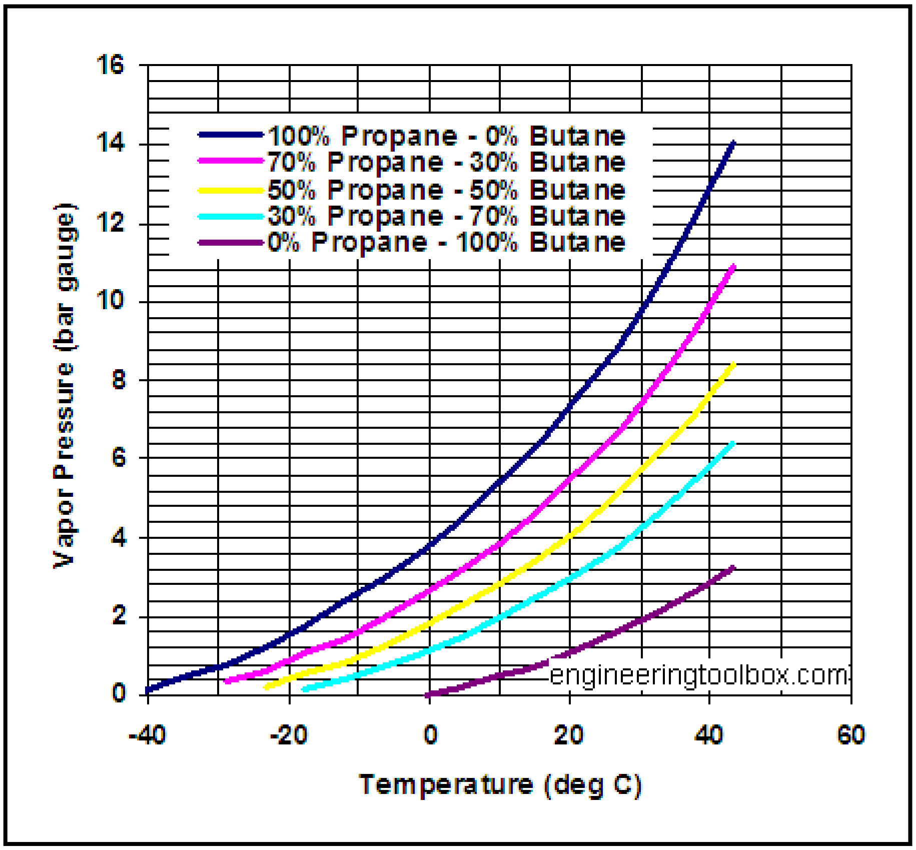

Figure 2.1 The Propane and Butane Mixture Diagram

Source: The Engineering Toolbox, 2012.

From Figure 2.1, vapor pressure of LPG with typical composition (30 % propane and 70 % butane) at surroundings' temperature of 20 ^{o}C is around 3 bar gauge (barg). If only this pressure is rapidly getting higher due to the escalating of surroundings' temperature, failure of the vessel might happen and possibilities of leaking to be happened are elevated.

Let's consider a worst case scenario where leakage of LPG took place. LPG in cylinder vessel may leak as a gas or a liquid. If the liquid leaks it will rapidly evaporate and form a quite large cloud of gas which will dive to the ground, as it is heavier than air. However, how much of LPG is considered necessary in order for an explosion to occur? A parameter called as flammability limit has helped to answer that question. Flammability limit is a range of percentage volume of any flammable gases where combustion or explosion might occur. So, if the percentage volume of leaked LPG is within this range, possible explosion can happen if there is air or O_2 and ignition present (Michelsen, 1992).

For decades, many researchers had done studies on how to minimize the flammability limit. As a result, it is found that addition of diluents can narrow down the range of flammability limit and indirectly lessen the risk of explosion to happen. Diluents usually make use of the inert gases such as neon (Ne), argon (Ar), xenon (Xe), nitrogen (N_2) and CO_2 with the purpose of helping to reduce the concentration of O_2 present ("Standard for Inert Gas Systems", 1984).

As for this study, CO_2 has been selected to be the diluents for LPG and air mixture because it is rather economical in cost if compared to other inert gases. Detail clarifications will be discussed in the becoming sub-section of this study (Bumgartner, n.d.).

2.2 LIQUEFIED PETROLEUM GAS (LPG)

In emergent world we are facing now, liquefied petroleum gas (LPG) is a practical source of energy as it emits less gases that can cause pollution such as nitrogen oxide (NO_x) and carbon monoxide (CO) (Razus *et al.*, 2009).

It can be categorized as a clean fuel as it also emits low percentage of CO_2 gas to the atmosphere and also has low sulphur contents that can be harmful to the environment. These facts thus providing a clean alternative energy in this age of rightful concern with environment safety and pollution control. It is a complete combustion fuel which reduces maintenance costs through the reduced plant and boiler downtime (Flogas, 2010).

2.2.1 Physical and Chemical Properties of LPG

LPG originally existed in gases form. It is then liquefied under certain pressure to be liquid form for storage and transportation purposes. This non-toxic fuel also carries many advantages to users such as minimal effect of corrosion towards equipments involved, environmental friendly as it consequences in clean burning as well as emits no contaminating gases and affect in low maintenance cost and time as it gives out no soot when burning and results to a longer life of equipments (TOTAL in India, n.d). Table 2.1 shows the list of some physical and chemical properties of LPG.

Table 2.1 Chemical and Physical Properties of LPG

PROPERTIES	DESCRIPTIONS	
Chemical Formula	C_3H_8,	C_4H_{10}
Molar Mass ($gmol^{-1}$)	44.0	58.0
Proportion (%)	30	70
Appearance	Colourless	
Odour	Pungent Odour – Ethyl Mercaptan (added)	
Solubility	Insoluble in water	
Boiling Point (^oC)	-44.5	
Vapour Pressure (kPa)	380 – 830	
Flash Point (^oC)	-104	
Auto Ignition Temperature (^oC)	510	
Flammability Unit (% vol.)	UFL = 8.5 LFL = 1.9	

Souce: Petronas Dagangan Berhad, 2004.

In addition to Table 2.1, LPG is also classified as non-toxic and non-carcinogen gas. However, if LPG is exposed to human, effect of overexposure might be asphyxiant and the target organs will be eye, skin and respiration system (Petronas Dagangan Berhad, 2004).

2.2.2 Storage, Handling and Transportation of LPG

In this sub-section, overall description is based on Malaysia Standard (MS) 830 which is the Code of Practice for The Storage, Handling and Transportation of Liquefied Petroleum Gases. According to MS 830, the domestic kind of LPG cylinder is classified as the 'portable container' which is designed to be readily moved, as distinguished from containers designed for stationary installations. Portable containers designed for transportation in such a manner that they can be safely transported in the filled or partly filled condition.

2.2.2.1 Storage

In specification of LPG storage cylinder, it shall be designed, fabricated and tested in accordance with MS 641 or MS 642 or other codes approved by the relevant authority. This scheme is also applied for the determination of its design pressure. In addition to this, marking must also be considered. Each container shall be conspicuously and permanently marked with the following information:

a. Manufacturer's name or trade-mark, serial number and year of manufacture
b. Pressure vessel code to which it is made
c. The water capacity in litres (L) or kilolitres (kL)
d. Class of vessel (e.g. Class 1)
e. Design pressure in kilopascals (kPa)
f. Date of initial hydrostatic test

g. Date of hydrostatic retest
h. The maximum safe working pressure in kilopascal (kPa)
i. The tare mass in kilograms (kg) of container (for containers to be filled by mass)
j. Official stamp of the inspecting authority

It is also specified that the containers of storage shall be equipped with openings suitable for the service for which the container is to be used. Such openings may be either in the container proper or in the manhole cover or part in one and part in the other. Connections for safety relief valves shall be located and installed in such a way in order to have direct communication with the vapour space whether the container is in storage or in use. If the containers located in a well inside the container with piping to the vapour space, the design of the well and piping shall permit sufficient safety relief valve discharge capacity. On the other hand, if they are located in a protecting enclosure, the enclosure shall be designed to protect against corrosion and allow inspection (MS 830, 2003).

In the installation requirement, LPG storage containers within a group shall be located so that their longitudinal axes are parallel to each other and preferably are directed away from any nearby storage of hazardous gases or flammable or combustible liquids. Cylindrical storage containers may be placed end to end with that the distance between the ends is not less than 3 meter or twice the diameter of the larger container, whichever is the greater. It is must also realized that storage containers shall not be installed one above the other as covered by MS 830 (2003).

Other than that, MS 830 (2003) has also stressed that the safety distance for LPG storage container must also be considered. Safety distances are intended to protect the LPG facilities from the radiation effects of fires involving other facilities as well as to minimize the risk of escaping LPG being ignited before being dispersed or diluted.

2.3 CARBON DIOXIDE (CO_2)

2.3.1 Physical and Chemical Properties of CO_2

Carbon dioxide (CO_2) was first discovered by a Scottish chemist and physician, Joseph Black, in 1750s. The linear molecule consists of a carbon atom that is doubly bonded to two oxygen atoms, O=C=O. It is an odourless and colourless gas which is slightly acidic and non-flammable (Lenntech Water Treatment and Purification, 2009).

Even though CO_2 mainly found in the gaseous form, it also has a solid and a liquid form. It can only be solid when temperatures are below -78 ^oC. Liquid CO_2 mainly exists when it is dissolved in water. CO_2 is only water-soluble, when pressure is maintained. After pressure drops, the CO_2 gas will try to escape to air. This results in the bubbles' forming into water. CO_2 can be found mainly in air, but also in water as a part of the carbon cycle CO_2 is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm (Shakhashiri, 2008). Table 2.2 shows extra information on physical and chemical properties of CO_2.

Table 2.2 Physical and Chemical Properties of CO_2

PROPERTIES	DATA
Molecular formula	CO_2
Molecular weight (g /mol)	44.01
Specific gravity (^oC)	1.53 at 21
Critical density (kg/m^3)	468
Concentration in air (ppm)	370.3×10^7
Stability	High

Liquid (kPa)	Pressure < 415.8
Solid (^oC)	Temperature < -78

Source: Lenntech Water Treatment and Purification, 2009.

In addition of the properties shown in Table 2.2, CO_2 has been used in various ways such as an ingredient in a carbonated drink to make it fizzy, as a component in producing lasers, a part of fire extinguisher substances and so much more. It is naturally exists in our environment in gases form. CO_2 is also classified as a green house gas as it can cause the green house effect where it absorbs some of the heat and trap it near the earth's surface, so that the earth is warmed up (Bumgartner, n.d.).

2.4 EFFECTS OF CO_2 ON FLAMMABILITY LIMITS OF LPG

Diluents acted as an important part in inerting process. Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen for the purpose of lowering the likelihood of explosion (Chen, 2009).

When an inert gas is added to a hydrocarbon gas/air mixture, the result is an increase in the lower flammable limit concentration and a decrease in the upper flammable limit concentration ("Standard for Inert Gas Systems", 1984). Figure 2.2 describes the effect of increasing in diluents in hydrocarbon gas-air mixture to flammability limit of hydrocarbon gases.

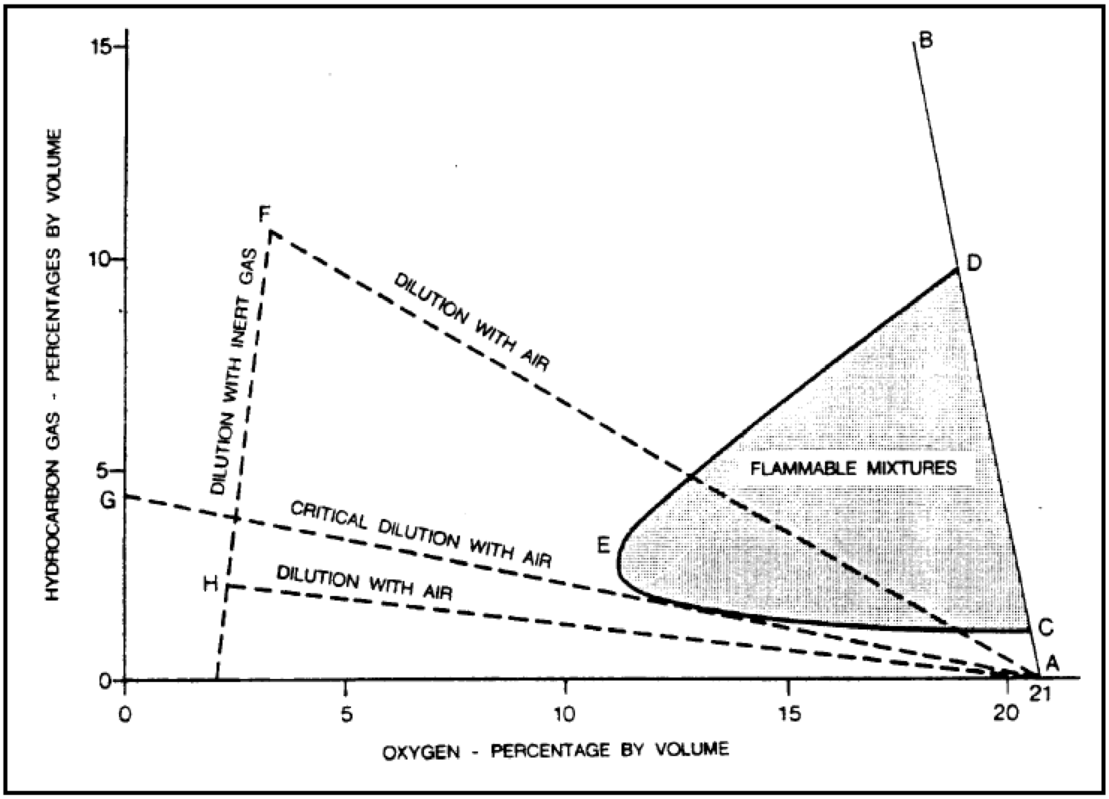

Figure 2.2 Hydrocarbon Gas/ Air/ Inert Gas Mixtures Effect on Flammability Limit

Source: "Standard for Inert Gas Systems", 1984

From Figure 2.2, hydrocarbon/air mixtures, without inert gas, lie on the line AB, the slope of which shows the reduction in O_2 content as the hydrocarbon content increases. Points to the left of AB correspond to mixtures whose O_2 content is further reduced by the addition of inert gas. As inert gas is added to hydrocarbon/air mixtures, the flammable range gradually decreases, until the O_2 content reaches a level (normally taken to be about 11 % by volume) at which no mixture can burn ("Standard for Inert Gas Systems", 1984).

From a study to predict the effects of the presence of diluents with methane on spark ignition engine performance conducted by Bade *et al.*, (2001), diluents were found especially good when the percentage of diluents in fuel is less than 50 %. The presence of a diluents with methane reduces the effective heating value of the fuel mixture when the energy released by the oxidation reactions of the fuel component is shared with the diluents. The energy released by combustion taken up by the CO_2 component was amplify drastically with temperature since the specific heat of CO_2 increased with temperature at a much greater rate than that for N_2 or air. These will tend to modify the composition of the final products of combustion. The effects of the presence of CO_2 were more obvious than that of N_2 (Bade *et al.*, 2001).

A professor from Canada said that the presence of CO_2 and N_2 as diluents with methane had lower down its effective heating value. Besides that, it has also reduced the flame speed of the mixture (Karim, 2010). Figure 2.3 shows a clearer proof on this.

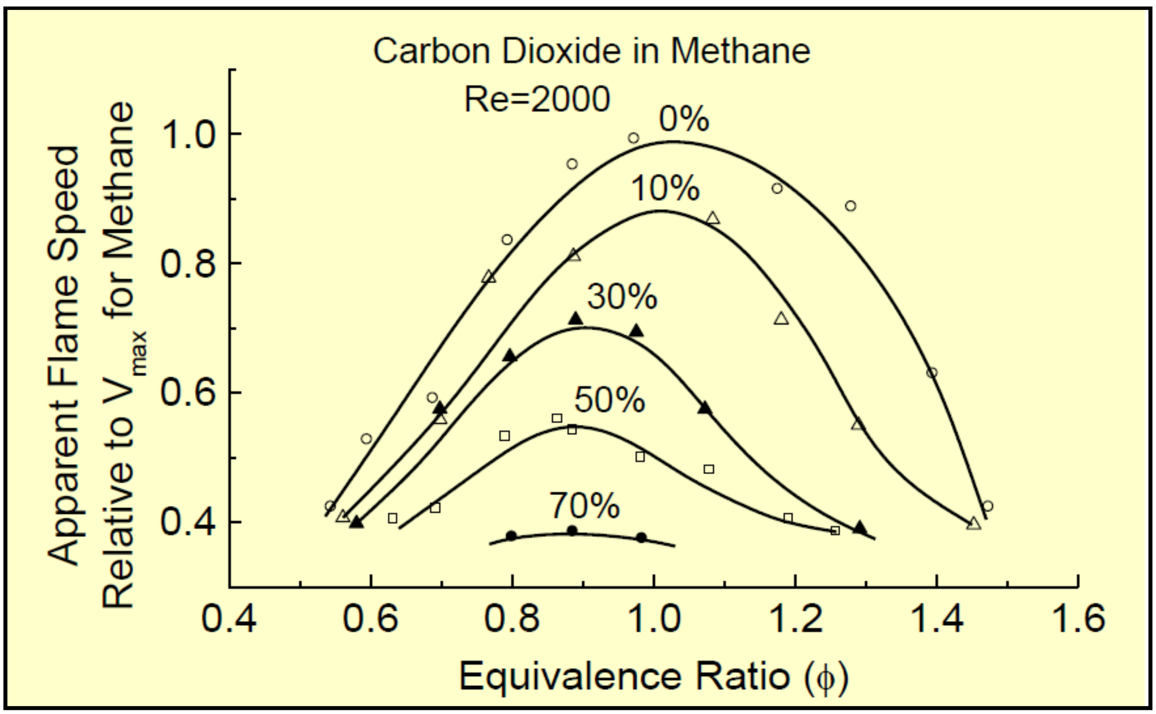

Figure 2.3 The Flame Propagation Rates within Flowing Mixtures Of Methane-CO_2-Air for a Flow Reynolds Number of 2000 and Different Volumetric Concentrations of CO_2- in the Methane.

Source: Karim, 2010